

# Piezoelectric and Optical Response of Uniaxially Stretched (VDF/TrFE) (75/25) Copolymer Films

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**Abstract.** The phase diagram of the poly(vinylidene fluoride-trifluorethylene) (P(VDF-TrFE)) copolymer system shows for VDF contents of 50...85 mol% a ferroelectric (FE)-paraelectric (PE) phase transition below melting temperature. Investigations on P(VDF-TrFE) 75/25 samples revealed a slight anisotropic behaviour, which leads to a strongly anisotropic stretching effect both on the phase transition and on the amount and nature of the FE phase in samples subjected to mechanical stretching along the main directions of the film.

In this work, both the refractive index  $n_{1,2}$  and the piezoelectric coefficient  $d_{33}$  of mechanically stretched P(VDF-TrFE) have been measured for samples with different levels of permanent deformation. These parameters are found to reflect the anisotropy of the permanently deformed samples. The stretching effect is most pronounced ( $n_{1,2}$ ) or limited ( $d_{33}$ ) to the vicinity of the yielding point of the material. Above the yielding point, almost the piezoelectric  $d_{33}$  coefficient of the non-deformed sample is observed for samples with large permanent deformation.

## Introduction

Vinylidene fluoride-trifluorethylene (VDF-TrFE) copolymers have attracted intense scientific and technological interest. Due to rather large piezo- and pyroelectric coefficients, P(VDF-TrFE) is widely used for several sensor and transducer applications. The scientific interest mainly originates from the ferroelectric phase transition, which occurs in P(VDF-TrFE) material at the phase transition temperature  $T_c$  below melting temperature  $T_m$ . Above  $T_c$ , the paraelectric phase with hexagonal crystalline structure is stable, which essentially consists of a statistical combination of TT, TG and TG' rotational isomers [1]. The Curie temperature was shown to strongly depend on VDF content [2,3], heat treatments [4,5], and poling procedure [6]. The ferroelectric – paraelectric phase transition at  $T_c$  involves conformational changes from the trans to gauche states, accompanied by a rotational motion of the chains around the chain axis. The crystalline structure in the ferroelectric phase is composed by all-trans chains with dipoles parallel to the  $b$ -axis. For VDF contents higher than 70 mol%, the ferroelectric transition is reversible and discontinuous [4]. Numerous studies have been carried out on high-energy electron irradiated P(VDF-TrFE) copolymers which show characteristic features of relaxor ferroelectrics [3].

Piezoelectricity in P(VDF/TrFE) copolymers originates both from the response of the crystalline volume and from the field induced motion of the interface separating crystalline and amorphous parts. In order to develop strategies for obtaining highly electroactive materials, it is thus important to understand conformational changes of the crystalline part induced by different external treatments of the material. In principle, a larger piezoelectric response should be observed in films with improved chain orientation and/or a more perfect crystalline phase. This in turn can be

achieved by, for example, mechanical stretching, annealing treatments above  $T_c$  and improved poling [6]. In this context, it would be interesting to investigate the effect of mechanical load, especially with respect to the transition temperature and structure of P(VDF/TrFE).

In order to obtain information about the relationship between structural changes and the nature of the paraelectric-ferroelectric transition, we have recently investigated the evolution of the ferroelectric – paraelectric phase transition of P(VDF-TrFE) 75/25 films with increasing permanent (plastic) deformation along the two main directions of the material. The slight anisotropic behaviour observed in the stress-strain curves of P(VDF-TrFE) 75/25 was related to the deformation effect on the phase transition temperature and the shape and height of the ferroelectric anomaly [7,8]. In this paper, we present data on the piezoelectric response and diffraction index of uniaxially stretched P(VDF-TrFE) 75/25 and discuss the results in the context of stress induced melting and re-crystallization processes in P(VDF-TrFE).

## Experimental

P(VDF/TrFE) 75/25 was obtained from PIEZOTECH S.A., Saint-Louis, France. Copolymer films with 100  $\mu\text{m}$  thickness were extruded, and several kV were applied to pole the films using the patented ISL-Bauer cycling process. Different permanent stretching levels were induced either along the direction of the extrusion (L) or perpendicular to it (T) with a Minimat (Polymer laboratories) testing machine in the tensile mode. The test velocity was  $dl/dt = 2 \text{ mm/min}$  on ca. 4 cm x 1 cm rectangular samples.

A capacitive micro-displacement meter was used to study the piezoelectric properties of the polymers. The measuring principle was developed by *Schmidt et al.* [9]. The electroded sample, situated between rounded tips, was subjected to sinusoidal electric excitation ( $U_{ac}=250\text{V}$ ,  $f=10\text{Hz}$ ). The capacitive probe, detecting the piezoelectric displacement  $x_3$  of the polymer, represented the frequency determining part of a vhf-oscillator ( $f_{vhf} \approx 100\text{MHz}$ ). The resulting frequency modulation of the vhf-oscillator was measured with a modulation analyzer HP 8901, and compared with the signal obtained from a quartz crystal connected mechanically in series with the sample. Analysis of results measured at several amplitudes  $U_{ac}$  revealed that the ratio  $d_{33}=x_3/U_{ac}$  is nearly independent of  $U_{ac}$ . This indicates that we deal with the linear piezoelectric regime and  $d_{33}$  represents the piezoelectric small signal coefficient of the polymer.

For the measurement of the refractive indices  $n_{1,2}$ , the experimental setup was a Mach-Zehnder interferometer whose light source is a diode laser pumped Nd:VO<sub>4</sub> laser with intercavity doubling to provide light at 532 nm. The interferometer is provided with a turntable capable of rotating the sample about a vertical axis and measuring the angle of rotation with a resolution of 5 minutes of arc. A photodetector counts the number of fringes as the sample is rotated starting from the normal incidence, permitting an accurate measurement of the optical thickness of the sample. Given the physical thickness of the sample the refractive indices ( $n_{1,2}$ ) of a P(VDF/TrFE) sample can be determined that are accurate to the third decimal place.

## Results and Discussion

X-ray diffraction experiments revealed a slight anisotropic structure in non-stretched P(VDF-TrFE) films [8]. The results indicate a preferential orientation of crystalline lamellar structures along the L-direction. This anisotropy manifests also in the quasi-static mechanical behaviour: Despite the fact that the yield stress (35 MPa) and the elastic moduli are almost the same in the L- and T-direction (the tangent modulus at 2% is  $0.73 \pm 0.1 \text{ GPa}$  in the L-direction and  $0.93 \pm 0.1 \text{ GPa}$  for the T-direction), the plastic range corresponding to the horizontal plateau of the stress-strain curve is much wider in the T-direction and a considerably larger maximum strain ( $\sim 400\%$ ) before mechanical failure is observed in this direction than for the L-direction ( $\sim 210\%$ ) [8]. Along the T-

direction, an initial localised deformation process leads to the formation of a neck. In the L-direction, the continuously increasing stress at higher strain level indicates work hardening probably due to the increased blocking of tied chains.

DSC scans for P(VDF-TrFE) (75/25) films after subjected to different levels of irreversible stretching show two peaks, corresponding to the FE-PE transition ( $T_c = 140\text{ }^{\circ}\text{C}$ ), and to the melting ( $T_m = 147\text{ }^{\circ}\text{C}$ ) [8,9]. Whereas no significant changes were observed for both transitions after stretching along the L-direction, stretching along the T-direction destabilizes the ferroelectric phase, leading to a decrease of  $T_c$  with permanent strain (Figure 1). On the other hand, the crystallinity of the polymer is not affected by the deformation.

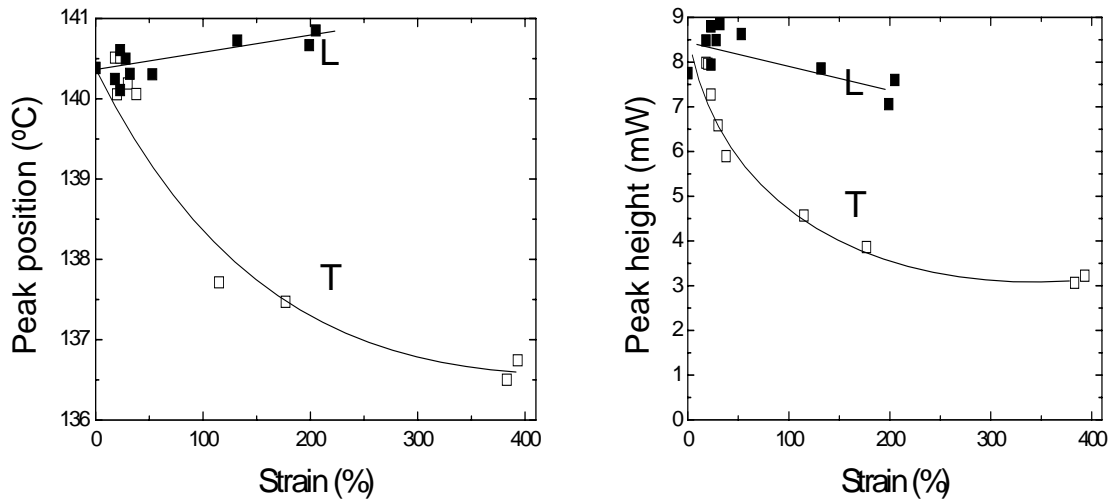


Fig. 1. Characteristic parameters of the DSC peak at the ferroelectric-paraelectric transition for samples deformed along the L- (black squares) and T-directions (open squares), respectively, as a function of strain level. Left: position of the peak in the temperature axis, right: intensity of the peak in the heat flux axis, taking into account a linear base line.

The piezoelectric coefficient  $d_{33}$  was measured for samples with various permanent deformations along the T- and L-direction, respectively. As it can be seen from the data plotted in Figure 2, longitudinal deformation does not significantly influence the piezoelectric response of the sample. However, we observe unusual piezoelectric behaviour for some samples with transversal deformation, which exhibit, as compared to the non-stretched film, either a strongly enhanced  $d_{33}$  coefficient or significantly reduced piezoelectric response. Note that the piezoelectric anomaly is restricted to the yielding region; for bigger permanent deformation in the T-direction, we measure  $d_{33}$  values quite similar to the non-deformed sample.

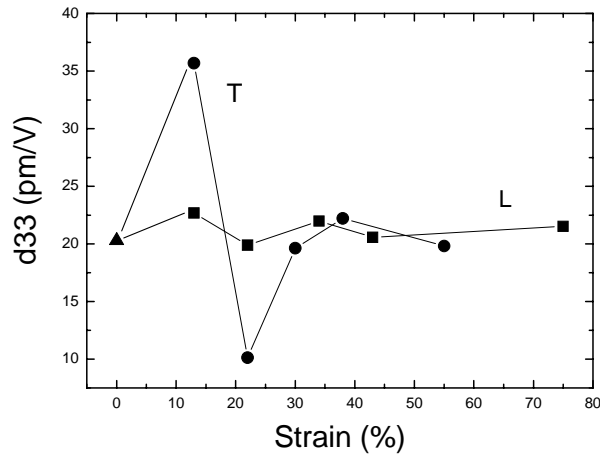


Fig. 2. Piezoelectric coefficient  $d_{33}$  for different levels of permanent deformation of P(VDF-TrFE). AC-voltage: 250 V; frequency 10 Hz. Black dots: deformation along the transversal direction; black squares: deformation along the longitudinal direction. The triangle corresponds to the un-stretched sample.

The refractive index  $n_{1,2}$  of stretched PVDF is depicted in Figure 3 for different degrees of permanent deformation. Again, the effect of longitudinal stretching is small. We observe refractive indices slightly decreasing with permanent strain level. The changes of optical properties induced by transversal stretching of the material are much more pronounced, especially in the yielding zone.

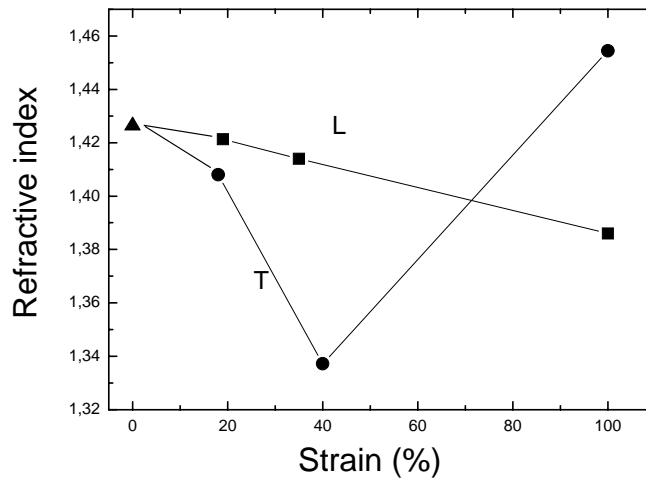


Fig. 3. Refractive index for P(VDF-TrFE) with different degrees of permanent deformation. Black dots: deformation along the transversal direction; black squares: deformation along the longitudinal direction. The triangles correspond to the un-stretched samples.

Differential scanning calorimetry studies provided information about the transition enthalpy of P(VDF-TrFE) and the degree of crystallinity. It was concluded that the crystalline parts of the original non-stretched film undergoes upon heating above  $T_c$  a complete transformation from the ferroelectric to the paraelectric structure [8]. For samples stretched along the L-direction, no significant changes are observed in both transitions (Figure 1), i.e. of the ferroelectric structure maintains even at high deformation levels parallel to the c-axis of the crystalline structure. Probably

only sliding between lamellae structures occurs, leaving the all-trans chain conformations and the CF<sub>2</sub> dipole orientation almost unchanged [8]. After stretching along the T-direction, however, significant changes of the transition peak occur (Figure 1) which indicate that the degree of ferroelectric ordering is reduced during the deformation. This should occur mainly by a reduction in the thickness of the lamellae structures, as the thermal anomalies do not indicate that bond defects were induced during stretching [8]. As the thinning of lamellae structures is apparently non-uniform, the crystalline phase in the T-stretched sample becomes heterogeneous. In addition, deformation along the T-direction induces dipole reorientation [8]. Interestingly, almost no alterations are found in the melting peak. There is evidence to suggest that the ferroelectric phase is transformed into a paraelectric phase, whereas the degree of crystallinity remains unchanged during the stretching process. The underlying mechanism may comprise melting and re-crystallisation [10]. The concept of the stress induced melting and re-crystallization of crystalline structures within the yielding range of L-stressed samples, proposed in a recent study [11], may explain the anomalies of the d<sub>33</sub> piezoelectric coefficient (Figure 2) and refractive index (Figure 3) in this region. Whereas stretching along the L-direction leads only to sliding between adjacent lamellar structures, T-stretching induces phase transformations, accompanied by large anomalies in the macroscopic response within the metastable region. Once the yielding range is passed, the piezoelectric response of the non-stretched material is almost retained. This indicates that chain rotation occurs mainly in the 1-2 plane and that the material properties along direction 3 do not suffer strong variations as a consequence of the process. Further, the amount of ferroelectric phase lost in the process still has a piezoelectric contribution by forming part of the interphase region between crystalline and amorphous phases. The contribution of this interface amounts in P(VDF-TrFE) to about 1/3 of the piezo-response of the material [11]. On the other hand, the refractive index, which is more sensitive to the particular orientation of dipoles and chains [12,13], changes irreversibly in the strained sample.

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